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Thermal broadening of the zero-phonon line in superfluid helium

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Based on the two-fluid model of helium II, a theory is proposed to explain the recently observed temperature dependence of the zero-phonon line (ZPL) in the optical spectra of Dy atoms in superfluid helium. According to this theory, the main reason for the observed dependence is the temperature redistribution of the normal and superfluid components of the liquid helium. It is also found that due to the Archimedes' principle, the linear vibronic interaction with long-wave phonons in the liquid phase is singularly enhanced. This enhancement, in turn, leads to a finite broadening of the ZPL of the superfluid component and a linear temperature dependence of the ZPL width of the normal component. The proposed theory allows us to explain the experimental results.

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I. INTRODUCTION

Recently, the optical spectrum of the inner-shell transition of the Dy atom in superfluid helium has been studied at various temperatures of the superfluid helium with high precision [1]. It was found that the spectrum contains a strong narrow zero-phonon line (ZPL) and a weak and broad phonon wing. The line has a width of 5.6 GHz at 1.48 K and 11.2 GHz at 2.12 K [1]. The phonon wing extends 400 GHz towards higher frequencies and has weak flat maxima at the roton and maxon frequencies. This structure of the observed spectrum was, in fact, expected [1,2]—the electrons of the inner shell are well isolated from the surrounding atoms by the outer electron shell of the Dy atom. Therefore the inner-shell transitions are characterized by a very weak vibronic interaction. The observed spectrum resembles the ZPL spectrum of the glyoxal molecule in the superfluid helium [3]; in this molecule, the valence electrons are strongly confined within the molecule, so the vibronic interaction with the surrounding helium atoms is also quite weak. However, it differs significantly from the observed optical spectra of valence electron transitions in rare-earth atoms [2,4] and alkaline-ionic ions in liquid helium [5–9]: these spectra, due to the stronger vibronic interaction, are broad and do not exhibit a narrow ZPL.

To explain the observed change in the ZPL width with temperature, the authors [1] used a model [10–12] commonly used for crystals. According to this model, the ZPL at zero temperature has a natural width. With increasing temperature, this line broadens due to the quadratic vibronic interaction. In the low-temperature limit, the main contribution to this broadening is made by this interaction with low-frequency acoustic phonons, which leads to the $\propto T^7$ dependence of the ZPL width on temperature T. Low-frequency pseudolocal modes can also contribute to the temperature broadening [12]. The observed difference in ZPL widths for 1.5 and 2.1 K was explained in [1] by these broadening mechanisms.

Liquid helium at the studied temperatures has a different amount of normal component, varying from 9% at 1.454 K to 80% at 2.124 K [13]. In [1] this is ignored, despite the fact that only this component has nonzero entropy causing the thermal broadening of the ZPL. In contrast to [1], we believe that in fact it is this difference in the content of the normal component of superfluid liquid helium that is the main reason for the difference in the ZPL width at the temperatures under study and not the quadratic vibronic interaction, as suggested in [1].

This paper presents a theoretical model of the optical spectra of impurity atoms in superfluid helium, which from the very beginning takes into account the presence of the superfluid and normal components in it. In this model the temperature dependence of the ZPL is a consequence of the temperature redistribution of these liquid components and the temperature dependence of the ZPL of the normal component. The ZPL shape of the superfluid component does not change with temperature, but its intensity decreases to zero as the temperature approaches the lambda temperature $T_\lambda = 2.17$ K.

Another significant change in our model is taking into account the difference between vibronic interactions with low-frequency phonons in the liquid and solid phases. Namely, the vibronic interaction in crystals tends to zero if the phonon frequency also tends to zero [11,12,14]. On the contrary, in liquids the vibronic interaction with these phonons increases when their frequency tends to zero. The reason for this difference lies in the Archimedes' principle, according to which any body submerged in a liquid is affected by a buoyant force that arises due to the fact that the submerged body displaces part of the liquid to its surface. Therefore a change in the distance to the nearest helium atoms surrounding the impurity atom during the electron transition in it (this change in Dy, as found in [2], is 0.15 Å) will eventually lead to a small but finite change in the total volume of the liquid. In

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macrocrystals, the change in the total volume does not occur. Since the change in the volume of the liquid occurs due to the linear vibronic interaction with phonons of almost zero frequency, this interaction in the liquid is incomparably stronger than in the crystal. The ultimate reason for this difference in the linear vibronic interaction in a liquid is related to the fundamental difference between a solid and a liquid in transverse modes: in a solid, they have a finite frequency at any wave number k, except $k = 0$, while in a liquid, the frequencies are 0 at any k of these modes. This allows the liquid to change its shape isochorically according to the Archimedes principle.

Here it is found that the linear vibronic interaction in a liquid increases singularly with a decrease in the phonon frequency. As a result of such increase in the vibronic interaction, a macroscopic amount of phonons with an almost zero frequency is created during the electron transition. This leads to a finite broadening of the ZPL in the spectrum already at the zero-temperature limit, when the liquid completely consists of the superfluid component. The width and the shape of the ZPL of the superfluid component remain unchanged with increasing temperature; its intensity tends to zero at lambda temperature. The width of the ZPL of the normal component existing at nonzero temperature increases linearly with increasing temperature. These theoretical results allow us to explain the results of ZPL measurements [1].

II. OPTICAL SPECTRUM

To describe the optical spectrum of the Dy atom, we use the Lax theory [15] of electronic transitions and take into account the linear vibronic interaction

$$V \equiv \hat{H}_2 - \hat{H}_1 = E_0 + \sum_k \omega_k^2 u_k x_k. \tag{1}$$

Here $\hat{H}_1$ and $\hat{H}_2$ are the vibrational Hamiltonians of the center in the initial (1) and final (2) electronic states, respectively, E_0 is the energy of the electronic transition, u_k is the change of the equilibrium position of the phonon coordinate x_k of the mode k during the transition, and ω_k is its frequency. In the harmonic approximation, the Fourier transform of the optical spectrum equals $e^{i\tilde{\omega}_0 t}F(t)$ [15], where $\tilde{\omega}_0 = \omega_0 + i\gamma_0$, $\omega_0 = (E_0 - E_S)/\hbar$ is the ZPL frequency, γ_0 is the natural linewidth,

$$\ln F(t) = \int d\omega \upsilon_\omega[(n_\omega + 1)(e^{i\omega t} - 1) + n_\omega(e^{-i\omega t} - 1)], \tag{2}$$

$\upsilon_\omega = \omega u_\omega^2 \rho(\omega)/2\hbar$ is the vibronic interaction of a phonon with frequency ω, u_ω is the change of the equilibrium position of this phonon at the transition, $n_\omega = (e^{\hbar\omega/k_B T} - 1)^{-1}$ is the Planck occupancy factor,

$$E_S = 2^{-1}\int d\omega \rho(\omega)\omega^2 u_\omega^2$$

is the Stokes loss, and $\rho(\omega)$ is the density of states of phonons.

Suppose that the atom is placed in the center of a spherical liquid. Then, for nondegenerate electronic states of atom in the long-wave limit, only $\propto r^{-1}\sin(kr)$ longitudinal modes contribute to the vibronic interaction (r is the distance to the origin). The change in the volume of the liquid due to the electronic transition in the atom can be expressed by $\Delta_V = 4\pi\langle R^2\Delta_R\rangle$, where

$$\Delta_R \propto R^{-1}\int_0^{a_0^{-1}} dk k^2 u_k \sin(kR) \tag{3}$$

is the change of the radius R of the liquid, a_0 is the atomic spacing in the liquid, and $\langle\ldots\rangle$ is the averaging over the R. Here we take into account that R can vary at different points on the surface of the sphere at several atomic lengths. Given that $\langle\cos(R/a_0)\rangle \simeq 0$, we find that Δ_{V} is finite in the limit of large R if $u_k \propto k^{-2}$, $k \to 0$. This gives, in the $\omega \to 0$ limit, $k \propto \omega$, $\rho(\omega) \propto \omega^2$, and $\upsilon_\omega \propto \omega^{-1}$. In crystals in the $\omega \to 0$ limit, $\upsilon_\omega \propto \omega$ [11,12,14]. Consequently, in liquids the linear vibronic interaction with low-frequency phonons is singularly enhanced in comparison with this interaction in crystals.

An important difference between liquids and crystals is that liquids, unlike crystals, do not have a well-defined upper limit of the phonon frequencies. We take this property of liquids into account by adding the cut-off factor $e^{-\omega/\varepsilon}$ in the phonon density of states of Debye. Then $\rho(\omega) = (\omega^2/2\varepsilon^3)e^{-\omega/\varepsilon}$, where $\varepsilon \sim \omega_m = 0.29$ THz is the maxon frequency. In this approximation,

$$\upsilon_\omega = \alpha\omega^{-1}e^{-\omega/\varepsilon}, \tag{4}$$

where $\alpha = E_S/\hbar\varepsilon$ is a dimensionless parameter of the linear vibronic interaction determined by the change in the overlapping integrals of the electronic wave functions of the Dy atom and the nearest helium atoms during the electron transition [15].

To estimate α, we use for the change in the distance to the nearest He atoms during the electronic transition in the impurity the value $\delta R \approx 0.15$ Å found in Ref. [2] (given that the relative intensity of ZPL is 0.7). To do this we present the Stokes loss in the form $E_S \approx \bar{\omega}^2 M_4 \delta R^2/2$, where M_4 is the mass of the helium atom, $\bar{\omega}$ is the mean frequency of vibrations of surrounding helium atoms, and we take into account that the half of the mean zero-point energy of these vibrations is equal to $M_4\bar{\omega}^2 A_0^2/2$, where $A_0 = \sqrt{\hbar/2M_4\bar{\omega}}$ is the mean amplitude of the zero-point vibrations of the helium atoms. We get $\alpha \approx (\delta R/A_0)^2$. Taking for $\bar{\omega}$ the mean frequency of the one-phonon wing 0.25 THz [2], we get $A_0 \approx 0.75$ Å, which gives $\alpha \approx 0.04$.

III. ZERO TEMPERATURE

In the case of $T = 0$, the Fourier transform satisfies the equation $\dot{F}_0/F_0 = -\alpha/(it - \varepsilon^{-1})$. Solving it, we get

$$F_0(t) = (1 - it\varepsilon)^{-\alpha}. \tag{5}$$

This function has a pole only in the lower part of the complex plane t. Therefore the optical spectrum $I(\Omega)$ differs from zero only for positive frequencies Ω ($\Omega = 0$ corresponds to the ZPL frequency). For small positive $\Omega \ll \varepsilon$ the main contribution to the spectrum comes from large t, giving $F_0 \approx (-it\varepsilon)^{-\alpha}$; for large $\Omega \gg \varepsilon$ it comes from small t, giving $F_0 \approx (1 - i\alpha\varepsilon t)^{-1}$. The corresponding spectra in the $\gamma_0 = 0$ limit are

$$\begin{aligned} I_0(\Omega) &\approx \alpha\varepsilon^{-\alpha}\Theta(\Omega)/\Omega^{1-\alpha}, \quad \Omega \ll \varepsilon, \\ I_0(\Omega) &\approx (\alpha\varepsilon)^{-1}e^{-\Omega/\alpha\varepsilon}, \quad \Omega \gg \varepsilon, \end{aligned} \tag{6}$$

where $\Theta(x)$ is the Heaviside step function. (A similar spectrum for small Ω was found in [16] for crystal lattices with one-dimensional phonons.) Consequently, the ZPL in a quantum liquid, in contrast to crystals, acquires a finite width already in the limit $T \to 0$, $\gamma_0 \to 0$. The reason for this is the singular enhancement of vibronic interaction with low-frequency phonons, which leads to the creation of a macroscopic number of phonons with almost zero frequency during the electronic transition.

The spectrum strongly depends on the vibronic interaction parameter α. The case $\alpha = 1$ is a border case: for $\alpha > 1$ the spectrum starts at zero, $I_0(\Omega \to 0) \to 0$, and for $\alpha < 1$ it starts with a stepped divergence, and the ZPL has a shape like a lambda letter. This case corresponds to the inner-shell transition of the Dy atom, studied in [1]. However, in this case the significant natural width $\gamma_0 \approx 5.15$ GHz hides the given shape.

In the case of large α, the moments of the spectrum $S_n = \varepsilon^n\alpha(\alpha+1)\ldots(\alpha+n-1)$, $(n = 1, 2, \ldots)$ are practically the same as in the case of the Poisson distribution (the first and second moments coincide): the larger α, the smaller the differences in the values of the moments. For example, with $\alpha = 10$, the third moments differ by 0.76%, the tenth moments by 55%; with $\alpha = 20$, the third moments differ by 0.22%, the tenth moments by 18%. Consequently, in the case of a strong vibronic interaction, the shape of the spectrum is close to Gaussian—the envelope of the Poisson distribution for a large number of occurrences α. This conclusion agrees with the results of measurement [2] of the emission spectrum of the $6s^2 - 6s6p$ transition of the valence electron in the Dy atoms at 1.5 K having FWHM ~ 1 THz (corresponds to $\alpha \sim 15$) and observed in [4] spectra of the $6s^2 - 6s6p$ singlet and triplet transitions of the valence electron in the Yb$^+$ ions in liquid helium.

IV. TEMPERATURE BROADENING OF ZPL

For $T_\lambda \geqslant T > 1$ K, the temperature dependence of the density of normal components [13,17–19] can be approximated as $\rho_N \approx [0.98 \times (T/T_\lambda)^{6.8} + 0.02]$. The density of superfluid component equals $\rho_S = 1 - \rho_N$. This component has zero entropy; the entropy of a normal liquid is nonzero and increases with temperature. Therefore the temperature broadening of the ZPL is completely due to the normal component. Taking this circumstance into account, the optical spectrum of the center should be represented in the form

$$I(\Omega) = \rho_S I_0(\Omega) + \rho_N(T) I_T(\Omega), \tag{7}$$

where the spectrum of the superfluid component $I_0(\Omega)$ is given by the Fourier transform of $F_0(t)$, while the spectrum of normal component $I_T(\Omega)$ is given by the Fourier transform of $F_T(t) = F_0(t)\exp(g_T(t))$, where

$$g_T(t) = \alpha \int_{-\infty}^{\infty} d\omega \upsilon_{|\omega|} n_{|\omega|} (\cos(\omega t) - 1) \tag{8}$$

is the temperature-dependent part of $\ln F$. Keeping the two largest terms in the limit $|t| \to \infty$, we get [20,21] $\ln F(t) = -\gamma_T|t| + i\varsigma\,\mathrm{sgn}(t)$, where $\gamma_T = \pi\alpha k_B T/\hbar$ describes the temperature broadening of the ZPL of a normal liquid, and $\varsigma = \pi\alpha/2$ is the asymmetry factor of ZPL. In the case of $\alpha \ll 1$ this factor can be neglected and we get

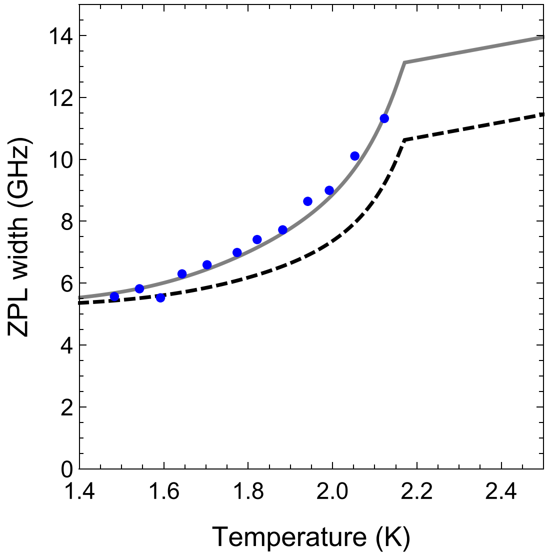

FIG. 1. Experimental (points, see [1]) and theoretical dependencies of the ZPL width of the Dy atoms in liquid helium with (solid line) and without (dashed line) account of the inhomogeneous broadening. The kinks at $T_\lambda = 2.17$ K are the result of a similar kink in the dependence of the density of the normal component on the temperature.

$$I(\Omega) \approx \frac{\rho_S \gamma_0 \pi^{-1}}{\Omega^2 + \gamma_0^2} + \frac{\rho_N \gamma_N \pi^{-1}}{\Omega^2 + \gamma_N^2}, \tag{9}$$

where $\gamma_N = \gamma_0 + \pi\alpha k_B T/\hbar$. The intensity of the first line $\propto \rho_S$ decreases to zero as the temperature rises to T_λ; its width remains unchanged. The intensity and width of the second line increase with increasing temperature, and the increase in width is linear.

In [1], to find the widths of the ZPL, a single-Lorentzian fit of the spectral shape was used. Therefore to compare the presented theory with the experiment, we also use a single-Lorentzian fit, using the nonlinear model fitting procedure [22]. Taking $\gamma_0 = 5.15$ GHz [1] and found above $\alpha = 0.04$, we get for the width of the normal component $\gamma_N = (5.15 + 2.5\,T)$ GHz (temperature in K). The temperature dependence of the ZPL width obtained in this case using a single-Lorentzian fit is consistent with the experiment for low temperatures, but at a higher temperature $T \approx 2$ K it gives about a 10% smaller value than in the experiment (see Fig. 1).

A possible reason for the discrepancy is that the different Dy atoms in the superfluid helium may have different configurations of the surrounding atoms, and hence the ZPL frequencies [23], which leads to inhomogeneous broadening of the ZPL. Note that in the case of an optical transition from 1S to 1P, characterized by a strong vibronic interaction, the differences in configurations can cause a rather large (~ 0.02 eV) broadening of the entire optical spectrum [24].

Following [23], we consider here that there are differences in the static (on the nanoscale timescale) configurations of the surrounding helium atoms and in the surface tension energy of the corresponding bubbles. The surface tension energy in the superfluid component acquires the most energetically favorable value. However, the thermal fluctuations of the normal component allow for different configurations and, consequently, different values of this energy for different Dy atoms, which leads to an inhomogeneous broadening of the ZPL. Given that the difference in surface energy of bubbles is small compared to k_BT, we can take the inhomogeneous broadening in the form $\Gamma\rho_N$, where Γ is a parameter. Then instead of γ_0 we get $\bar{\gamma}_0 = \gamma_0 + \Gamma\rho_N$. Assuming $\Gamma = 2.5$ GHz, we obtain the temperature dependence of the ZPL width of the Dy atoms in good agreement with the experiment (see Fig. 1).

Note that the theoretical value of $\alpha = 0.04$ with an accuracy of several percent coincides with the value of this parameter, which gives the best match of the theoretical curve with the experimental points when using α and Γ as the fitting parameters. The value of $\gamma_0 = 5.15$ GHz is taken from [1]. Therefore, in fact, the dashed line in Fig. 1 is calculated without fitting the parameters, and the solid line corresponds to a one-parameter fit of the theory to the experiment.

V. SUMMARY

A theory is proposed that describes the optical spectra of impurity atoms in superfluid helium, based on a two-fluid model of helium II. In this theory the temperature dependence of the spectrum is a consequence of the temperature redistribution of these two fluids and the temperature dependence of the spectrum of the normal fluid component. It is shown that, owing to the Archimedes principle, the linear vibronic interaction with low-frequency phonons in the liquid phase is singularly enhanced. The reason for this enhancement is due to the zero values of the transverse phonon frequencies in a liquid, which allows the liquid to change its shape isochorically in accordance with the Archimedes' principle. As a result of such a singular increase in the vibronic interaction, a macroscopic amount of phonons with an almost zero frequency is created during the electron transition, which leads to a finite broadening of the ZPL in the spectrum already at the zero-temperature limit. It is shown that the temperature dependence of the ZPL has a discontinuity in the derivative at the lambda temperature $T_\lambda = 2.17$ K, and above T_λ this dependence becomes linear.

Theory is applied for the description of the temperature dependence of ZPL of the optical spectrum studied in [1] of the inner-shell transition of the Dy atom in superfluid helium. A good agreement of the theory with experiment is achieved, taking into account, in addition to the linear vibronic interaction, the inhomogeneous broadening of ZPL considered earlier in [23], caused by slow fluctuations of the surface tension of the bubbles of the surrounding helium atoms.

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